RECIRCULATING ANODE

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1.   Field of the Invention.

This invention relates generally to the field of particle-based electrochemical power sources, and, more specifically, to the maintenance of a recirculating flow of a reaction solution through the anodes of metal-based fuel cells.

2.   Related Art.

Particle-based electrochemical power sources, including without limitation metal-based fuel cells, are emerging as an attractive alternative to traditional energy sources. In metal-based fuel cells, when metal anodes within the cell cavities are exposed to an electrolysis agent such as hydroxide, an electrochemical reaction takes place whereby the metal releases electrons, and a reaction product is formed, typically one or more ions or oxides of the metal. Through this process, the metal anodes are gradually consumed. The released electrons flow through a load to a cathode, where they react with a second reactant such as oxygen. .

Particle-based electrochemical power sources, including without limitation metal-based fuel cells, which employ particulate anodes and which deliver reaction agents such as hydroxides to the anodes through a reaction solution pose particular challenges since, for such power sources (e.g., fuel cells) to function efficiently, it is necessary to recirculate the reaction solution throughout and within the particulate anodes so that the appropriate electrochemical reaction can take place. However, as the electroactive (e.g., metal) particles in the anode beds are consumed during the electrochemical reaction, they become smaller and smaller, and can become more densely packed together. The dense packing of the small particles can lead to particle buildup, clogging and interference with, and resulting reduction of, the flow of reaction

solution throughout and within the particulate anodes. This in turn can lead to the generation of insoluble reaction products, which can further clog the flow of reaction solution throughout the cell. The result is typically a substantially less efficient fuel cell.

5   In a zinc-based fuel cell, for example, clogging caused by the generation of small particles can lead to the following electrochemical reaction occurring at the anode beds:

$$Zn + 2OH^- \rightarrow Zn(OH)_{2(s)} + 2e^- \qquad (1)$$
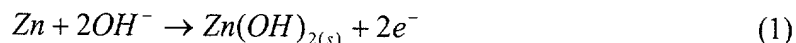
The reaction product $Zn(OH)_{2(s)}$, unlike $Zn(OH)_4^{2-}$, is insoluble.

In prior developments of particle-based electrochemical power sources (e.g., metal-based fuel cells employing metal particles), the problem of small particle buildup 10 is either not recognized or inadequately addressed. In one such development, illustrated by U.S. Patent No. 5,434,020, Cooper, a tapered cell cavity is proposed to achieve a low packing density of the particles. Electrolyte is allowed to enter or exit the tapered end, but there is no indication in Cooper that the narrow end permits or is configured to permit the release of small particles to prevent buildup.

15   In another such development, illustrated by U.S. Patent No. 3,847,671, Leparulo, et al., a slurry of metal particles in an electrolyte is introduced into a cell cavity, and retained until the fuel cell has discharged. No mention is made of maintaining anode bed porosity under anodic dissolution, recirculating solution through the cell cavity, or allowing small particles to escape from the cell cavity during anodic dissolution.

20   In a further such development, illustrated by "The C.G.E. Circulating Zinc-based Battery: A Practical Vehicle Power Source," A.J. Appleby and M. Jacquier, Journal of Power Sources, Vol. 1, pp. 17-24, 1976/1977, and "Charge-Discharge Behavior of the C.G.E. Circulating Zinc-Air Vehicle Battery," A.J. Appleby, J. Jacquelin, and J.P. Pompon, Society of Automotive Engineers, International Automotive Engineering, 25 Congress and Exposition, Cobo Hall, Detroit, Feburary 28 – March 4, 1977, a metal slurry is continuously pumped into a cell cavity which has a cathode, but which lacks an anode bed formed of the particulate material. That is, the anodic metal particles are constantly in rapid motion and/or suspended in the metal slurry. Since a particulate anode bed is not maintained, the problems of maintaining porosity of the anode bed or a 30 substantially uniform flow of fluid through the anode bed are not addressed.

In an additional such development, illustrated by U.S. Patent No. 3.887.400, Doniat, et al., a cell cavity is disclosed which lacks an anode bed formed of the particulate material. Consequently, this reference also fails to address the problems of maintaining porosity of the anode bed or a substantially uniform flow of fluid through 5 the anode bed.

In USP 6,296,958, a fluid mechanical device is discussed for introducing fluidized particulate material into the fuel cell cavity, but this patent does not address the problem of maintaining the anode bed porosity at a sufficiently high state that an adequate electrolyte flow is maintained through the bed.

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SUMMARY

The invention provides a power source for a particle-based electrochemical power source. The power source has one or more cells, each comprising a particulate anode and a cathode. A flow path delivers a flow of reaction solution through the 15 particulate anode within a cell. The particulate anode forms a quasi-static bed of particles. One or more particle releasers are positioned along the flow path, each configured to allow metal particles which are likely to cause clogging to exit the cell. By allowing these particles to be released from the cell, the particle releasers maintain the particulate anode in a sufficiently porous state and allow a sufficient flow of reaction 20 solution through the anode to enable efficient operation of the fuel cell.

Other systems, methods, features and advantages of the invention will be or will become apparent to one with skill in the art upon examination of the following figures and detailed description. It is intended that all such additional systems, methods, features and advantages be included within this description, be within the 25 scope of the invention, and be protected by the accompanying claims.

RELATED APPLICATIONS

This application is related to U.S. Patent Application Serial No. To Be Determined, entitled "METHODS OF PRODUCING OXYGEN REDUCTION 30 CATALYST," Howrey Dkt. No. 04813.0022.NPUS00. filed October 9, 2001; U.S.

Patent Application Serial No. To Be Determined, entitled "METHODS OF USING FUEL CELL SYSTEM CONFIGURED FOR PROVIDING POWER TO ONE OR MORE LOADS," Howrey Dkt. No. 04813.0026.NPUS00, filed on even date herewith; U.S. Patent Application Serial No. To Be Determined, entitled "MANIFOLD FOR

5   FUEL CELL SYSTEM," Howrey Dkt. No. 04813.0027.NPUS00, filed on even date herewith; U.S. Patent Application Serial No. To Be Determined, entitled "FUEL CELL SYSTEM," Howrey Dkt. No. 04813.0028.NPUS00, filed on even date herewith; and U.S. Patent Application Serial No. To Be Determined, entitled "POLYMER COMPOSITES, CATHODES, AND SYSTEMS THEREOF," Howrey Dkt. No.

10   04813.0025.NPUS00, filed on even date herewith. Each of these applications are owned in common by the assignee hereof, and each is hereby fully incorporated by reference herein as though set forth in full.

BRIEF DESCRIPTION OF THE DRAWINGS

15   The components in the figures are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention. In the figures, like reference numerals designate corresponding parts throughout the different views.

FIG. 1 is a block diagram of an embodiment of a metal fuel cell.

FIG. 1A is an alternative block diagram of a metal-based fuel cell.

20   FIG. 2 is a front view of a first embodiment of an individual cell within the power source of a metal-based fuel cell illustrating a flow path for a flow of reaction solution through the particulate anode.

FIG. 3A is a view along 2-2 in FIG. 2, illustrating a particular embodiment of a particle releaser according to the invention.

25   FIG. 3B is a view along 2-2 in FIG. 2, illustrating a second embodiment of a particle releaser according to the invention.

FIG. 3C is a top view of the particle releaser of FIG. 3B.

FIG. 4 is a front view of a second embodiment of an individual cell within the power source of a metal-based fuel cell employing one or more fluid mechanical

30   devices.

FIG. 5 is a flowchart of an embodiment of a method according to the invention.

DETAILED DESCRIPTION

5   Advantages of Particle-Based Electrochemical Power Sources

An advantage of particle-based electrochemical power sources relative to traditional power sources such as lead acid batteries is that they can be refueled, and therefore are capable of providing energy over a longer duration of time than lead acid batteries. In a zinc-based fuel cell, for example, a fuel in the form of zinc or zinc-coated

10   particles in a potassium hydroxide solution can be maintained in storage, and a discharged fuel cell can be replenished simply by removing the spent potassium hydroxide and zincate reaction product, and providing the fresh zinc particles in potassium hydroxide solution into the cell cavities. The zinc particles then form particulate beds within the cell cavities which function as the anodes.

15   Another advantage of these particle-based power sources is that they are regenerative, meaning that the reaction products and spent reaction solution thereof can be processed to form metal which can be reintroduced back into the fuel cells to replenish the anode beds as they are consumed by the electrochemical reaction. In the case of the zinc-based fuel cell, for example, the spent reaction solution may consists of

20   zincate dissolved in potassium hydroxide. If the zincate is allowed to precipitate into zinc oxide, the spent reaction solution consists of zincate, zinc oxide, and potassium hydroxide and possibly zinc hydroxide. This spent reaction solution can be reprocessed back into zinc particles and fresh potassium hydroxide which can be reintroduced into the cell cavities during a next refueling cycle.

25   Particle-based electrochemical power sources other than metal-based fuel cells (e.g., zinc-based fuel cells) are suitable to enjoy the advantages of and to be practiced in accordance with the invention. These particle-based electrochemical power sources can be characterized in that they utilize electroactive particles other than metal or metal-coated particles to form the anode of the power source. Examples of

non metallic particulate power sources are particles of sodium borohydride, sodium thiosulfate, oxalic acid, phosphorus, and manganese hydroxide.

Introduction to Particle-Based Electrochemical Power Sources

A block diagram of an embodiment 100 of a particle-based electrochemical power source is illustrated in Figure 1. As illustrated, the particle-based electrochemical power source comprises a power source 102, an optional reaction product storage unit 104, an optional regeneration unit 106, a fuel storage unit 108, and an optional second reactant storage unit 110. The power source 102 in turn comprises one or more cells each having a cell body defining a cell cavity, with an anode and cathode situated in each cell cavity. The cells may be coupled in parallel or series. In one implementation, they are coupled in series to form a cell stack.

The anode flowing through the cell cavities comprises the fuel (e.g., electroactive particles) stored in fuel storage unit 108. In accordance with the invention, one suitable flow of anodes (i.e., electroactive particles (e.g., metal or metal-coated particles, and the like, including without limitation zinc and zinc-coated particles)) through the cell cavities of a particle-based electrochemical power source (e.g., metal-based fuel cells, and the like, including without limitation zinc-based fuel cells) comprises a static or quasi-static flow. As employed herein, "quasi-static flow" refers to a flow rate of the electroactive particles through the cell cavity that is significantly less than the flow rate of the electrolyte fluid carrier for such electroactive particles (as measured by its superficial velocity) through the cell cavity, and "static flow" refers to a flow rate of such electroactive particles that is not greater than about zero (and can be negative). In one implementation, the flow rate of electroactive particles through the cell cavity, measured as $0.3 \ cm^3/s$, is not faster than one tenth of the flow rate of the electrolyte fluid, as measured by its superficial velocity through the cell cavity. The superficial velocity can be calculated, among other ways, by dividing the flow rate of the electrolyte fluid by the cross-sectional area of the cell cavity(ies) (assuming no particles are present) through which the electrolyte fluid passes.

In order to facilitate efficient function of, and/or to limit substantially nonuniform accumulation of reaction products within the cell cavity(ies) of, a particle-

based electrochemical power source utilizing a flowing anode bed, it can be desirable to maintain a predetermined porosity through the flowing anode bed. In one aspect, this can be suitable where the particles of the flowing anode bed are not fully (i.e. 100%) consumed by dissolution or disintegration (e.g., via premature clogging/packing of the particles that can limit dissolution and/or disintegration) in the electrolyte reaction solution (e.g., KOH solution). Suitable predetermined porosities include without limitation porosities, ε, greater than about 0.4, or greater than about 0.2, or greater than about 0, or in the range(s) from about 0.4 to about 0.8, where ε is the volume of the cell cavity not occupied by the electroactive particles divided by the total volume of the cell cavity. This measure of porosity, ε, can be calculated, among other ways, by utilizing the equation $\varepsilon = (1 -$ electroactive particle packing density), where the electroactive particles packing density is calculated by dividing the dry weight of the electroactive particles in each appropriate section (e.g., cell cavity) by the weight of a volume of pure electroactive particles equal to the volume of that section. As can be readily determined, the smaller the size of the electroactive particles, the greater the electroactive particles packing density, and the less the porosity. Suitable porosities can be achieved, among other ways, by configuring the cell cavity with one or more particle releaser(s) to permit relatively small electroactive particles to exit the cell. Suitable particle releasers can be in suitable regular and irregular geometric shapes, and include without limitation structures that permit particles that are likely to cause clogging of the cell cavity to exit the cell (e.g., lips, or segmented lips, on the cell wall, sieves, mesh, and the like, and suitable combinations of any two or more thereof); structures that reduce the gap at the exit of the cell to a dimension in the range(s) from about 100% to about 150% of the average longest dimension of an electroactive particle (e.g., diameter for a spherical particle); structures that jut out from the wall of the cell at the exit of the cell by a dimension in the range(s) from about 150% to about 200% of the average longest dimension of an electroactive particle (e.g., diameter for a spherical particle); and the like; and suitable combinations of any two or more thereof.

Within the cell cavities of power source 102, an electrochemical reaction takes place whereby the flowing anode bed releases electrons, and forms one or more reaction products. The electrons released from the electrochemical reaction at the anode flow through a load to the cathode, where they react with one or more second reactants from optional second reactant storage unit 110 or from some other source. This flow of electrons through the load gives rise to an overpotential (i.e., work) required to drive the demanded current, which overpotential acts to decrease the theoretical voltage between the anode and the cathode. This theoretical voltage arises due to the difference in electrochemical potential between the anode (Zn potential of -1.215V versus standard hydrogen electrode (SHE) reference at open circuit) and cathode (O_2 potential of +0.401V versus SHE reference at open circuit). When the cells are combined in series, the sum of the voltages for the cells forms the output voltage of the power source.

The one or more reaction products can then be provided to optional reaction product storage unit 104 or to some other destination. The one or more reaction products, from unit 104 or some other source, may then be provided to optional regeneration unit 106, which regenerates fuel and/or one or more of the second reactants from the one or more reaction products. The regenerated fuel can then be provided to fuel storage unit 108, and/or the one or more second reactants can then be provided to optional second reactant storage unit 110 or to some other destination. As an alternative to regenerating the fuel from the reaction product using the optional regeneration unit 106, the fuel can be inserted into the system from an external source and the reaction product can be withdrawn from the system.

The optional reaction product storage unit 104 comprises a unit that can store the reaction product. Exemplary reaction product storage units include without limitation one or more tanks, one or more sponges, one or more containers, one or more vats, one or more barrels, one or more vessels, and the like, and suitable combinations of any two or more thereof. Optionally, the optional reaction product storage unit 104 is detachably attached to the system.

The optional regeneration unit 106 comprises a unit that can electrolyze the reaction product(s) back into fuel (e.g., electroactive particles, including without

limitation metal particles and/or metal-coated particles, and the like) and/or second reactant (e.g., air, oxygen, hydrogen peroxide, other oxidizing agents, and the like, and suitable combinations of any two or more thereof). Exemplary regeneration units include without limitation water electrolyzers (which regenerate an exemplary second reactant (oxygen) by electrolyzing water), metal (e.g., zinc) electrolyzers (which regenerate a fuel (e.g., zinc) and a second reactant (e.g., oxygen) by electrolyzing a reaction product (e.g., zinc oxide (ZnO)), and the like, and suitable combinations thereof. Exemplary metal electrolyzers include without limitation fluidized bed electrolyzers, spouted bed electrolyzers, and the like, and suitable combinations of two or more thereof. The power source 102 can optionally function as the optional regeneration unit 106 by operating in reverse, thereby foregoing the need for a regeneration unit 106 separate from the power source 102. Optionally, the optional regeneration unit 106 is detachably attached to the system.

The fuel storage unit 108 comprises a unit that can store the fuel (e.g., for particle-based electrochemical power sources, such as metal fuel cells, metal (or metal-coated) particles or liquid born metal (or metal-coated) particles or suitable combinations thereof). Exemplary fuel storage units include without limitation one or more tanks (for example, without limitation, a plastic or other inert material tank for holding potassium hydroxide (KOH) and metal (e.g., zinc (Zn), other metals, and the like) particles, and the like), one or more sponges, one or more containers (e.g., a plastic container for holding dry metal (e.g., zinc (Zn), other metals, and the like) particles, and the like), one or more vats, one or more barrels, one or more vessels, and the like, and suitable combinations of any two or more thereof. Optionally, the fuel storage unit 108 is detachably attached to the system.

The optional second reactant storage unit 110 comprises a unit that can store the second reactant. Exemplary second reactant storage units include without limitation one or more tanks (for example, without limitation, a high-pressure tank for gaseous second reactant (e.g., oxygen gas), a cryogenic tank for liquid second reactant (e.g., liquid oxygen) which is a gas at operating temperature (e.g., room temperature), a tank for a second reactant which is a liquid or solid at operating temperature (e.g., room

temperature), and the like), one or more sponges, one or more containers, one or more vats, one or more barrels, one or more vessels, and the like, and suitable combinations of any two or more thereof. Optionally, the optional second reactant storage unit 110 is detachably attached to the system.

5   In one embodiment, the particle-based electrochemical power source is a metal-based fuel cell. The fuel of a metal-based fuel cell is a metal that can be in a form to facilitate entry into the cell cavities of the power source 102. For example, the fuel can be in the form of metal (or metal-coated) particles or liquid born metal (or metal-coated) particles or suitable combinations thereof. Exemplary metals for the metal (or metal-

10   coated) particles include without limitation zinc, aluminum, lithium, magnesium, iron, sodium, and the like.

In this embodiment, when the fuel is optionally already present in the anode of the cell cavities in power source 102 prior to activating the fuel cell, the fuel cell is pre-charged, and can start-up significantly faster than when there is no fuel in the cell

15   cavities and/or can run for a time in the range(s) from about 0.001 minutes to about 100 minutes without additional fuel being moved into the cell cavities. The amount of time which the fuel cell can run on a pre-charge of fuel within the cell cavities can vary with, among other factors, the pressurization of the fuel within the cell cavities, and alternative embodiments of this aspect of the invention permit such amount of time to be in the

20   range(s) from about 1 second to about 100 minutes or more, and in the range(s) from about 30 seconds to about 100 minutes or more.

Moreover, the second reactant optionally can be present in the fuel cell and pre-pressurized to any pressure in the range(s) from about 0.01 psi gauge pressure to about 200 psi gauge pressure prior to a an outage sense time after the controller sensing the

25   power outage condition to facilitate the fuel cell's start-up in a timeframe significantly faster than when there is no second reactant present and no pre-pressurization in the fuel cell prior to the optional controller sensing the power outage condition. Optionally, the one or more second reactants are present in the power source 102 at a time prior to an outage sense time, which outage sense time is in the range(s) from about 10

30   microseconds to about 10 seconds after the controller has sensed demand of primary

power from (for use of the power source as a primary power source), or outage of primary power external to the power source (for use of the power source as a backup/auxiliary power source), the one or more loads.

Moreover, in this embodiment, one optional aspect provides that the volumes of one or both of the fuel storage unit 108 and the optional second reactant storage unit 110 can be independently changed as required to independently vary the energy of the system from its power, in view of the requirements of the system. Suitable such volumes can be calculated by utilizing, among other factors, the energy density of the system, the energy requirements of the one or more loads of the system, and the time requirements for the one or more loads of the system. In one embodiment, these volumes can vary in the range(s) from about 0.001 liters to about 1,000,000 liters.

In one aspect of this embodiment, at least one of, and optionally all of, the metal fuel cell(s) is a zinc-based fuel cell in which the fuel is in the form of fluid borne zinc particles immersed in a potassium hydroxide (KOH) electrolytic reaction solution, and the anodes within the cell cavities are particulate anodes formed of the zinc particles. In this embodiment, the reaction products may be the zincate ion, $Zn(OH)_4^{2-}$, or zinc oxide, ZnO.

In this embodiment, the one or more second reactants can be an oxidant (for example, oxygen (taken alone, or in any organic or aqueous (e.g., water-containing) fluid (for example and without limitation, liquid or gas (e.g., air)), hydrogen peroxide, and the like, and suitable combinations of any two or more thereof). When the second reactant is oxygen, the oxygen can be provided from the ambient air (in which case the optional second reactant storage unit 18 can be excluded), or from the second reactant storage unit 18. Similarly, when the second reactant is oxygen in water, the water can be provided from the second reactant storage unit 18, or from some other source, e.g., tap water (in which case the optional second reactant storage unit 18 can be excluded). In order to replenish the cathode, to deliver second reactant(s) to the cathodic area, and to facilitate ion exchange between the anodes and cathodes, a flow of the second reactant(s) can be maintained through a portion of the cells. This flow optionally can be maintained

through one or more pumps (not shown in Figure 1), blowers or the like, or through some other means.

In this embodiment, the particulate anodes are gradually consumed through electrochemical dissolution. In order to replenish the anodes, to deliver KOH to the anodes, and to facilitate ion exchange between the anodes and cathodes, a recirculating flow of the zinc particles can be maintained through the cell cavities. This flow can be maintained through one or more pumps (not shown) applied to deliver fluid borne zinc particles from the fuel storage tank 108 to the cell cavities, or through some other means.

As the potassium hydroxide contacts the zinc anodes, the following reaction takes place at the anodes:

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^- \tag{2}$$
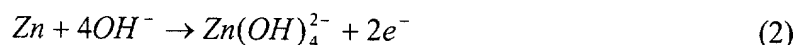
The two released electrons flow through a load to the cathode where the following reaction takes place:

$$\frac{1}{2}O_2 + 2e^- + H_2O \rightarrow 2OH^- \tag{3}$$
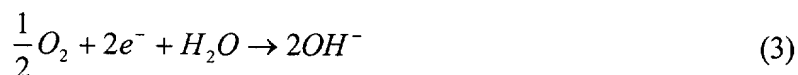
The reaction product is the zincate ion, $Zn(OH)_4^{2-}$, which is soluble in the reaction solution KOH. The overall reaction which occurs in the cell cavities is the combination of the two reactions (2) and (3). This combined reaction can be expressed as follows:

$$Zn + 2OH^- + \frac{1}{2}O_2 + H_2O \rightarrow Zn(OH)_4^{2-} \tag{4}$$
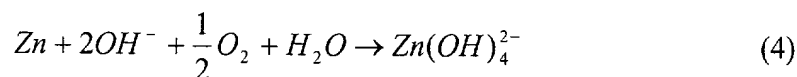
Alternatively, the zincate ion, $Zn(OH)_4^{2-}$, may be allowed to precipitate to zinc oxide, ZnO, a second reaction product, in accordance with the following reaction:

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^- \tag{5}$$
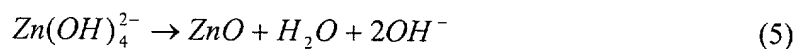
In this case, the overall reaction which occurs in the cell cavities is the combination of the three reactions (2), (3), and (5). This overall reaction can be expressed as follows:

$$Zn + \frac{1}{2}O_2 \rightarrow ZnO \tag{6}$$

Under real world conditions, the reactions (5) or (6) yield a voltage potential of about 1.4V. For additional information on this embodiment of a zinc-based battery, the

reader is referred to U.S. Patent Nos. 5,952,117; 6,153,329; and 6,162,555, which are hereby incorporated by reference herein as though set forth in full.

The reaction product $Zn(OH)_4^{2-}$, and also possibly ZnO, can be provided to reaction product storage unit 104. Optional regeneration unit 106 can then reprocess these reaction products to yield oxygen, which can be released to the ambient air or stored in second reactant storage unit 110, and zinc particles, which can be provided to fuel storage unit 108. In addition, the optional regeneration unit 106 may yield water, which may be discharged through a drain or stored in second reactant storage unit 110. It may also regenerate hydroxide, OH‾, which may be discharged or combined with potassium to yield the potassium hydroxide reaction solution.

The regeneration of the zincate ion, $Zn(OH)_4^{2-}$, into zinc and one or more second reactants, may occur according to the following overall reaction:

$$Zn(OH)_4^{2-} \rightarrow Zn + 2OH^- + H_2O + \frac{1}{2}O_2 \qquad (7)$$
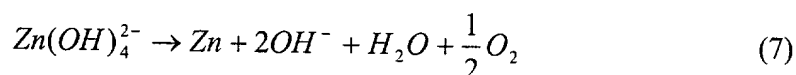
The regeneration of zinc oxide, ZnO, into zinc and one or more second reactants may occur according to the following overall reaction:

$$ZnO \rightarrow Zn + \frac{1}{2}O_2 \qquad (8)$$

It should be appreciated that embodiments of metal fuel cells other than zinc fuel cells or the particular form of zinc fuel cell described above are possible for use in a particle-based electrochemical power source according to the invention. For example, aluminum fuel cells, lithium fuel cells, magnesium fuel cells, sodium fuel cells, iron fuel cells, and the like are possible, as are metal fuel cells where the fuel is not in particulate form but in another form such as sheets or ribbons or strings or slabs or plates. Embodiments are also possible in which the fuel is not fluid borne or continuously recirculated through the cell cavities (e.g., porous plates of fuel, ribbons of fuel being cycled past a reaction zone, and the like). It is also possible to avoid an electrolytic reaction solution altogether or at least employ reaction solutions besides potassium hydroxide, for example, without limitation, sodium hydroxide, inorganic alkalis, alkali or alkaline earth metal hydroxides. See, for example, U.S. Patent No. 5,958,210, the entire

contents of which are incorporated herein by this reference. It is also possible to employ metal fuel cells that output AC power rather than DC power using an inverter, a voltage converter, and the like.

In another embodiment, the particle-based electrochemical power source is a particle-based electrochemical power source that has one, or any suitable combination of two or more, of the following properties: the power source optionally can be configured to not utilize or produce significant quantities of flammable fuel or product, respectively; the power source can provide backup power to one or more loads for an amount of time limited only by the amount of fuel present (e.g., in the range(s) from about 0.01 hours to about 10,000 hours or more, and in the range(s) from about 0.5 hours to about 650 hours, or more); the power source optionally can be configured to have an energy density in the range(s) from about 35 Watt-hours per kilogram of combined fuel and electrolyte added to about 400 Watt-hours per kilogram of combined fuel and electrolyte added; the power source optionally can further comprise an energy requirement and can be configured such that the combined volume of fuel and electrolyte added to the system is in the range(s) from about 0.0028 L per Watt-hour of the system's energy requirement to about 0.025 L per Watt-hour of the system's energy requirement, and this energy requirement can be calculated in view of, among other factors, the energy requirement(s) of one or more load(s) comprising a system including the power source (In one embodiment, the energy requirement of the system can be in the range(s) from 50 Watt-hours to about 500,000 Watt-hours, whereas in another embodiment, the energy requirement of the system can be in the range(s) from 5 Watt-hours to about 50,000,000 Watt-hours); the power source optionally can be configured to have a fuel storage unit that can store fuel at an internal pressure in the range(s) from about – 5 pounds per square inch (psi) gauge pressure to about 200 psi gauge pressure. In one implementation, this particle-based electrochemical power source comprises a metal-based fuel cell that, in one embodiment, is a zinc-based fuel cell.

Figure. 1A is a block diagram of an alternative embodiment of a metal-based fuel cell in which, compared to Figure 1, like elements are referenced with like identifying numerals. Dashed lines are flow paths for the recirculating anode fluid when the

optional regeneration unit is present and running. Solid lines are flow paths for the recirculating anode fluid when the fuel cell system is running in idle or discharge mode. As illustrated, in this embodiment, when the system is operating in the discharge mode, optional regeneration unit 106 need not be in the flow path represented by the solid lines.

5   An advantage of particle-based electrochemical power sources relative to traditional power sources such as lead acid batteries is that they can provide longer term primary and/or auxiliary/backup power more efficiently and compactly. This advantage stems from the ability to continuously refuel the particle-based electrochemical power sources using fuel stored with the fuel cell, from some other source, and/or regenerated

10   from reaction products by the optional regeneration unit 106. In the case of the zinc-based fuel cell, for example, the duration of time over which energy can be provided is limited only by the amount of fuel which is initially provided in the fuel storage unit 108, which is fed into the system during replacement of a fuel storage unit 108, and/or which can be regenerated by the optional regeneration unit 106 from the reaction products that

15   are produced. Thus, a system, comprising at least one particle-based electrochemical power source that comprises an optional regeneration unit 106 and/or a replaceable and/or refillable fuel storage unit 108, can provide primary and/or auxiliary/backup power to the one or more loads for a time in the range(s) from about 0.01 hours to about 10000 hours, or even more. In one aspect of this embodiment, this system can provide

20   back-up power to the one or more loads for a time in the range(s) from about 0.5 hours to about 650 hours, or even more. Moreover, such a system can optionally be configured to expel substantially no reaction product(s) outside of the system (e.g., into the environment).

Embodiments of the Invention

25   Figure 2 is a front view of an embodiment of an individual cell 200 within the power source 102 of a metal-based fuel cell. A particulate anode 208 is maintained within a cell cavity 204 of the cell. Within the cell cavity 204, the particulate anode undergoes electrochemical dissolution when exposed to a reaction solution. A flow path for a recirculating flow of the reaction solution is provided through the anode. In

30   the particular embodiment illustrated in Figure 2, the flow path extends from top to

bottom through the anode, and is represented by the vertical arrows within cell cavity 204. Reaction solution (and also optionally metal particles of original size for the purpose of replenishing the particulate anode 208) enters the cell at orifice 214, proceeds along conduit 216, and is distributed into the cell by flow distributor 206.

5   From flow distributor 206, the flow path extends into and through the particulate anode 208, to the bottom 210 of the cell. From the bottom 210 of the cell, the flow path extends along conduit 212 and exits the cell at orifice 218.

A cross section 300 of one embodiment of cell 200 is illustrated in Figure 3A. This cross section represents the view 2-2 in Figure 2. As shown, the cross-section is

10   formed of a planar laminate arrangement of layers. The particulate anode is identified with numeral 208. To the immediate right of the particulate anode 208 is a metal current collector 308 embedded in a cell frame 302. In one implementation, the cell frame is a plastic cell frame. To the immediate left of the particulate anode 208 is a separator 304, which, in one implementation, is made of a polymer (e.g.,

15   polypropylene). To the left of the separator 304 is gas diffusion cathode 306, which, in one implementation, is a carbon and teflon or PTFE gas diffusion electrode. An exemplary embodiment of a polymer composite electrode which can serve as gas diffusion electrode 306 is disclosed in U.S. Patent Application Serial No. To Be Determined, Howrey Dkt. No. 04813.0025.NPUS00, filed concurrently herewith,

20   which is hereby fully incorporated by reference herein as though set forth in full. Embedded in the leftmost portion of cathode 306 is a metal mesh which, in one implementation, is a nickel mesh.

The layers are preferably of a planar form to facilitate stacking of individual cells in series to form a cell stack. In such an arrangement, the rightmost surface of

25   cell body 302 from a cell 300 is placed in contact with the leftmost surface of the cathode 306a from the adjacent cell 300a (shown in phantom in Figure 3A). In the particular embodiment shown in Figure 3A, the rightmost surface of cell body 302 is configured to have alternating contact surfaces 320 and voids 319, and it is the contact surfaces 320 which are placed in contact with the cathode 306a. The voids 319 are

30   filled with ambient air to facilitate the passage of oxygen into the interior of the

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cathode as required by the aforementioned reaction (3) which occurs within the cathodes.

The current collector 308 is electrically coupled to the metal mesh 316a within the cathode 306a of the adjacent cell 300a through one or more metal pins or rods 314. (The cathode 306a of the adjacent cell is shown in phantom in Figure 3A.) These pins or rods allow current to pass left to right from one cell to the next, which are stacked on top of one another to form a cell stack.

Alternatively, in lieu of current collector 308 and metal pins or rods 314, the cell body 302 would be made of graphite or a composite of plastic and carbon or plastic and metal particles of sufficient quantity that the plastic composite conducts electricity.

The separator 304 is porous to allow potassium hydroxide reaction solution to pass from the particulate anode 208 to the cathode 306. In addition, the cathode 306 allows the passage of oxygen into its interior to allow the aforementioned reaction (3) to occur. In Figure 3A, one entry point of oxygen into cathode 306a is identified with numeral 318. In addition, as discussed, the voids 319 in the rightmost portion of the cell body 302 facilitate the entry of oxygen into the interior of the cathodes.

Referring to Figure 3A, conduit 212 is in communication through-flow channel 312 with the portion of the cell cavity that is occupied by the particulate anode 208. A particle releaser 310 is configured within the cell body 302. When particles are first placed in the portion of the cell cavity, they fall to the bottom of the cell cavity and form bridges across the cavity walls by virtue of the reduction of bed thickness due to particle releaser 310. As anodic dissolution occurs, the particles decrease in size, and the bridges collapse. The particle releaser 310 allows these particles to flow through the flow channel 312 and be released from the cell cavity into conduit 212, whereupon they exit the cell through the flow of the reaction solution. Depending on the characteristics of the particle releaser 310, some particles of original size can be also allowed to flow through the flow channel 312 and exit the cell.

Referring to Figure 1, upon exiting the cell cavity, the reaction solution containing the small particles and the reaction products of the electrochemical reactions which occur during fuel cell operation may be sent to zinc fuel and electrolyte reservoir 108, and then recirculated back into any of the cell cavities within the power source 102 through any of orifices 114. Alternatively, they may be sent to reaction product storage unit 104, and then to regeneration unit 106, where they may be reprocessed into fresh reaction solution, one or more second reactants, and particles of original size. Fresh reaction solution and (optionally) metal particles of original size may then be reintroduced back into any of the cell cavity within the power source 102 through any of orifices 114.

In one implementation, the thickness 324 of the portion of the cell cavity confining the particulate anode is nominally about three times the original diameter of the electroactive (e.g., metal) particles, and the particle releaser 310 is configured such that the width 322 of the flow channel 312 is slightly greater than the original diameter of the electroactive (e.g., metal) particles. For example, for an original particle diameter of .6 mm, the thickness 324 of the portion of the cell cavity confining the particulate anode is nominally about 2 mm. The thickness 322 of the flow channel is about .85 mm in this example.

A cross section 330 of a second embodiment of cell 200 is illustrated in Figure 3B. Again, this cross section represents the view 2-2 of the cell 200 in Figure 2. As with the previous embodiment, the cross-section is formed of a planar laminate arrangement of layers comprising from left to right cathode 306, separator 304, particulate anode 208, and current collector 308 embedded in a cell frame 302. The individual features of these layers have been previously described and need not be repeated except insofar as to discuss differences with the previous embodiment, which relate to the particle releaser 332 within the cell body 302.

In this embodiment, particle releaser 332 is formed of a screen, a top view of which is illustrated in Figure 3C. The screen is in communication with the interior of the cell cavity through the openings 340 in the screen, which form a flow channel with conduit 212. As illustrated in Figure 3C, each opening 340 has a long axis 344

and a short axis 342. The short axis 342 of the openings 340 in the screen can be approximately equal to the original diameter of the particles, and the long axis can equal or exceed the short axis. In one example, for particles having an original diameter of .6 mm, the long axis 344 of each opening 340 is about 1 mm, and the

5   short axis 342 is about .6 mm. In this example, the thickness 324 of the cell cavity can be about 2 mm.

The particle releaser in any of the foregoing embodiments can be configured to release a sufficient number of particles so that the interparticle porosity of the anode and the flow rate of reaction solution through the anode are sufficient to

10   facilitate efficient operation of the particle-based electrochemical power source (e.g., fuel cell) and/or to limit accumulation of reaction products within the cell cavity. In one embodiment employing zinc particles and a potassium hydroxide reaction solution, the porosity ε of the particulate anode can be maintained in the range of about 0.4 to about 0.8, where ε is the volume of the cell cavity not occupied by the

15   zinc particles divided by the total volume of the cell cavity (e.g., (1 − zinc packing density (as calculated per above)), and the superficial velocity (as calculated per above) of potassium hydroxide reaction solution through the anode should be maintained in the range of about 10 to about 200 cm/min., in order to maintain efficient operation of the zinc-based fuel cell.

20   A second embodiment of cell 200 is illustrated in Figure 4. This embodiment is identical to the embodiment illustrated in Figure 2, except that flow distributor 206 here includes a plurality 222 of fluid mechanical devices for allowing at least a portion of the reaction solution (and optionally particulate material) flowing along flow path 220 to enter the cell cavity, with the remainder exiting the cell cavity

25   through orifice 224. As explained in U.S. Patent No. USP 6,296,958, which is hereby fully incorporated herein by reference, the fluid mechanical devices should be configured in such a way that vortices are created in the spaces between adjacent ones of the fluid mechanical devices. These vortices draw reaction solution and optionally particulate material flowing along flow path 222 in a substantially uniform manner.

A flowchart of one embodiment of a method of operation of a metal-based battery cell according to the invention is illustrated in Figure 5. As illustrated, in step 500, a flow of reaction solution is provided through a particulate anode in the cell cavity while anodic dissolution occurs through one or more electrochemical reactions.

5   Step 502 occurs concurrently or subsequently to step 500. In step 502, particles that are likely to clog the anode are released from the cell cavity. In one embodiment, through the foregoing steps, the porosity of the anode and the flow rate through the anode are maintained sufficiently to enable efficient battery operation.

As utilized herein, the term "about" is intended to allow some leeway in mathematical exactness to account for tolerances that are acceptable in the trade, e.g., any deviation upward or downward from the value modified by "about" by any value in the range(s) from 1% to 20% of such value.

As employed herein, the term "in the range(s)" comprises the range defined by the values listed after the term "in the range(s)", as well as any and all subranges contained within such range, where each such subrange is defined as having as a first endpoint any value in such range, and as a second endpoint any value in such range that is greater than the first endpoint and that is in such range.

As utilized herein, the term "significantly faster" comprises any increase in the time value modified by "significantly faster" that is in the range(s) greater than 10% of such time value. The term "significant" typically means at a value at least in the range(s) greater than 10% of the number modified by "significant".

EXAMPLE

A zinc-based cell of the type shown in Figure 3A was constructed, with the thickness 324 of the anode bed being 2 mm, and the thickness 322 of flow channel

25   312 being .85 mm. The particulate anode was originally formed of zinc particles .6 mm in diameter. A potassium hydroxide reaction solution was used. The cell was operated at 120 amps for 16 hours with no deterioration in cell voltage or flow of electrolyte through the bed. The cell was then disassembled and the bed examined. The bed was divided up into nine sections, and the zinc pellets in each section were

30   dried and weighed. The dry weight of the zinc in each section was then divided by

the weight of a volume of pure zinc equal to the volume of the section. This calculation resulted in the zinc packing density for the section. The porosity ε of each section was then determined from the zinc packing density for the section as follows: $\varepsilon = (1 - \text{zinc packing density})$. The following table compiles the results of these

5   measurements for the nine sections:

$\varepsilon = 0.71$	$\varepsilon = 0.57$	$\varepsilon = 0.75$
$\varepsilon = 0.71$	$\varepsilon = 0.59$	$\varepsilon = 0.76$
$\varepsilon = 0.81$	$\varepsilon = 0.76$	$\varepsilon = 0.78$

        While various embodiments of the invention have been described, it will be apparent to those of ordinary skill in the art that many more embodiments and implementations are possible that are within the scope of this invention. In particular

10   and without limitation, the invention encompasses metal-based fuel cells other than zinc-based fuel cells, e.g., aluminum/air fuel cells, embodiments in which the flow path of the reaction solution through the cell cavity is other than from top to bottom, e.g., horizontal or non-vertical, embodiments in which particle releasers other than those specifically shown and described are used, and embodiments in which the cells

15   are other than planar, e.g., tapered or sloped cells.